

## Chemical characteristics of lead-zinc ores from North Vietnam, with a special attention to the In contents

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**Abstract:** In order to find In-rich sphalerite, Pb-Zn ores hosted in Paleozoic sedimentary rocks including abundant carbonates were studied chemically in the northernmost Vietnam, because both high-temperature In-anomaly and low temperature MVT (Mississippi Valley type) genesis, which could be contradictory, have been proposed in the mineralized terrane. A large variety of Pb-Zn ores was found by this study, such as (1) REE-rich (up to 1,210 ppm) galena-sphalerite subtype (Na Son), which is rhyolite-related with a high-temperature alteration assemblage, (2) In-Fe-rich sphalerite>galena-pyrrhotite subtype (Na Bop and Cho Dien), which is reduced and high temperature type, (3) In-Fe-poor sphalerite>galena subtype (Lang Hich, Mi Tic and Phudo), and (4) Fe-sphalerite> galena-rhodochrosite (Cuc Duong) subtype. The latter two subtypes are considered to have formed by low-temperature hydrothermal solutions.

In the Bac Kan region, economically important In-anomalous value was recognized on the Pb-Zn ores from Na Bop mine and weak anomaly in the Cho Dien ores. These ores are composed of Fe-rich sphalerites with pyrrhotite occurring in and around the Cho Dien Dome close to syenite dikes. The In-bearing ore deposits can be formed with high temperature ore solution liberated from hidden fractionated “tin” granitic intrusion of the ilmenite series in the Cho Don area and possibly below center of the Cho Dien Dome, and may have been formed under the highest temperature and reduced condition among the Pb-Zn mineralizations. The highest In-value is In<sub>sp</sub> of 391 ppm and Zn concentrates value of 898 ppm, both of which are considered to be economical.

### 1. Introduction

Lead-zinc mineralization occurs mostly in Paleozoic sedimentary terranes in the northernmost Vietnam. The major provinces are Ha Giang, Bac Kan, and Tuyen Quang. During the course of sheet mapping, 73 ore deposits and showings have been recognized in these provinces. Most of these deposits are small to medium in size, but the total ore reserves reaches to 97 million tons (Tran *et al.*, 2009). The Paleozoic sedimentary terrain in the northernmost Vietnam is a continuous part of the southern China plate (Fig. 1), where located are large In-bearing Pb-Zn deposits of the Dulong and Dachang mines (Ishihara and Murakami, 2008) and deformed MVT (Mississippi Valley type) Pb-Zn deposits at Huize (Han *et al.*, 2007). Indium anomalies of up to 1,000 ppm were already reported from the ores of Cho Dien area by ESCAP (1990, p. 70).

A reconnaissance study was made on the Pb-Zn ores

collected during a short visit of the summer of 2007, and found anomalous high In-sp values (calculated In in sphalerite from bulk ore analyses) up to 2,603 ppm in the storage ores from Na Bop mine, Cho Don (market Don), and up to 646 ppm in those from the Dien mine, Cho Dien (Ishihara *et al.*, 2009). These In-anomalies are observed with high-temperature mineral assemblages including black sphalerite, pyrrhotite, arsenopyrite and Sn minerals.

Another Pb-Zn ore samples studied were collected by Y. Watanabe during a short visit in a JICA program in 2000, from Ba Bo and Na Tum mines, Cho Don area, from Sy Binh iron mine, south of the Ngason area, and from Me Tic and Cuc Duong mines of the Thai Nguyen region. These ores are often carbonate hosted, which are considered a Mississippi Valley type (Watanabe, 2000). The samples were also taken from Na Bop, Cho Dien, Lang Hich and Na Son mines in Bac Kan, Thai Nguyen and Ha Giang regions (Fig. 1) through the framework of the Vietnamese National Research Project code

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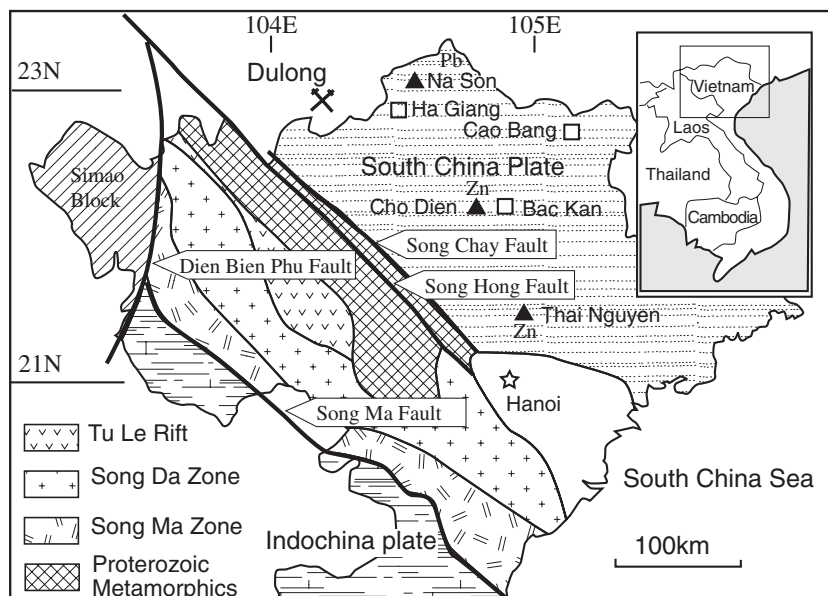


Fig. 1 Tectonic framework of the northern Vietnam and location of the studied Pb-Zn mineralized regions.

KC.08.24/06-10". The total numbers of the studied samples are 44.

The collected samples were crushed by stamp mill at the Institute of Geological Sciences, VAST (Vietnamese Academy of Science and Technology) and at the Geological Survey of Japan, and grinded by ceramic and agate mortars. Therefore, no tungsten contamination is expected in the powdered samples. The chemical analyses were performed at Activation Labs, Canada, adopting TD (total digestion), then ICP-MS method. Pb-rich ores were also analyzed by the code 8 method. The results are shown in Appendices 1 to 3.

## 2. Geological Background

The lead-zinc mineralized province of northeastern Vietnam, is underlain by the Paleozoic sedimentary terrain of South China Plate. Mesozoic volcanic and granitic rocks intrude locally into these rocks and give them thermal metamorphism and hydrothermal mineralization. The studied ore deposits are located in the following three mining fields of Ha Giang (Fig. 1), and Bac Kan and Thai Nguyen (Fig. 2). Representative analyzed samples are shown in Plates I and II.

### 2.1 Ha Giang region

In this region, Pb-Zn deposits are known to occur as veins in Paleozoic terrigenous carbonate sedimentary rocks and intruded alkaline igneous rocks. The largest one of Na Son deposit, which is called here as Na Son subtype, is

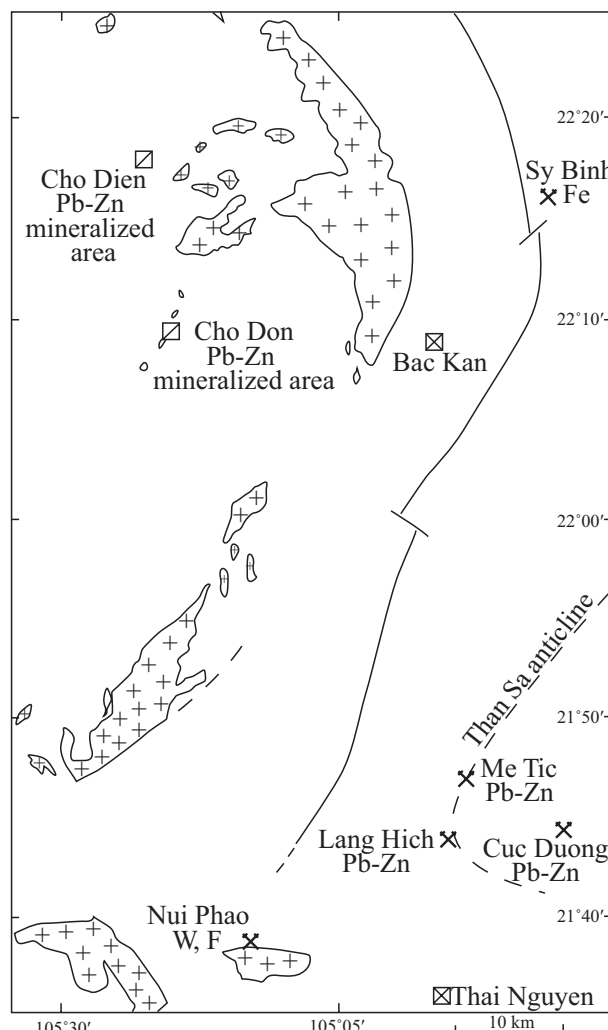


Fig. 2 Locality map of the studied Pb-Zn deposits hosted in Paleozoic sediments (compiled from Tuyen Quang, (Long, P.D. edit., 2001) and Bac Kan sheets, Tinh, H. X. edit., 2001).

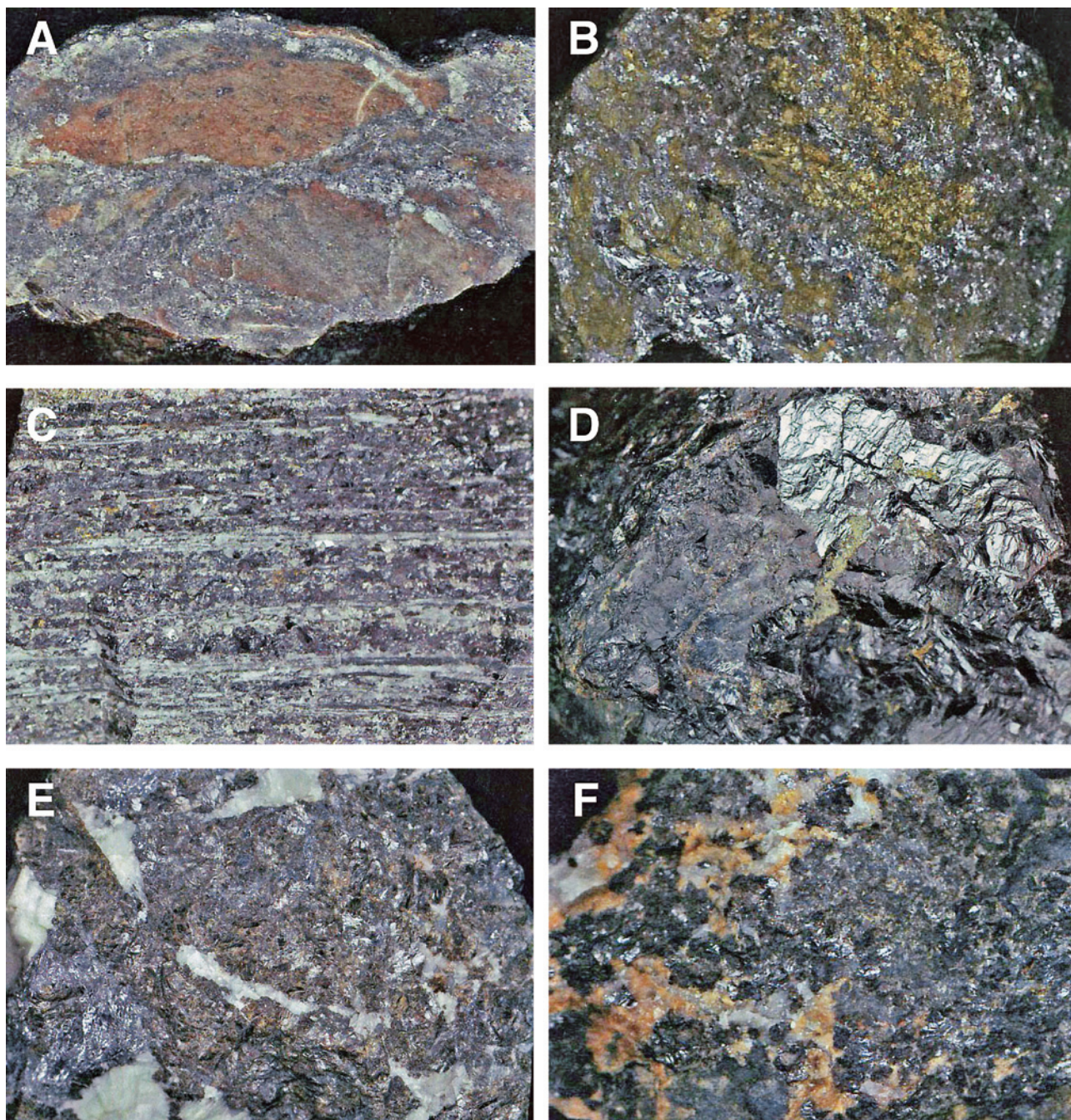


Plate I Studied Pb-Zn ores from representative mine. The scale is shown by the height in mm.  
 A: Galena>sphalerite filling fractures of altered rhyolite, Na Son mine (Na Son-36). 32 mm.  
 B: Galena-dark brown sphalerite-pyrrhotite-chalcopyrite ore from Na Bop mine (8080613). 32 mm.  
 C: Banded black sphalerite ore from Na Bop mine (8081614). 42 mm.  
 D: Dark colored sphalerite from the Cho Dien mine. Shiny part is cleavage of the sphalerite (8081605). 43 mm.  
 E: Brown sphalerite-calcite (white) ore from Phudo mine (8081618). 48 mm.  
 F: Sphalerite(black)-rhodochrosite (yellow) vein from Cuc Duong mine (CD-1). 35 mm.

located in alkaline rhyolitic and small syenitic intrusion of Triassic age. Galena is more abundant than sphalerite; both filling fractures in the altered rhyolite (Plate 1A); thus the mineralization is later than the rhyolite intrusion. This study indicates a fair amount of REE-bearing minerals occurring in

the Na Son ores, implying that this mineralization is related to the host rhyolitic activities.

The orebodies are 50 to 300 m long and 0.5 to 10 m thick. The ore minerals are disseminated in altered and fractured host rocks, and/or occur in quartz veins. The

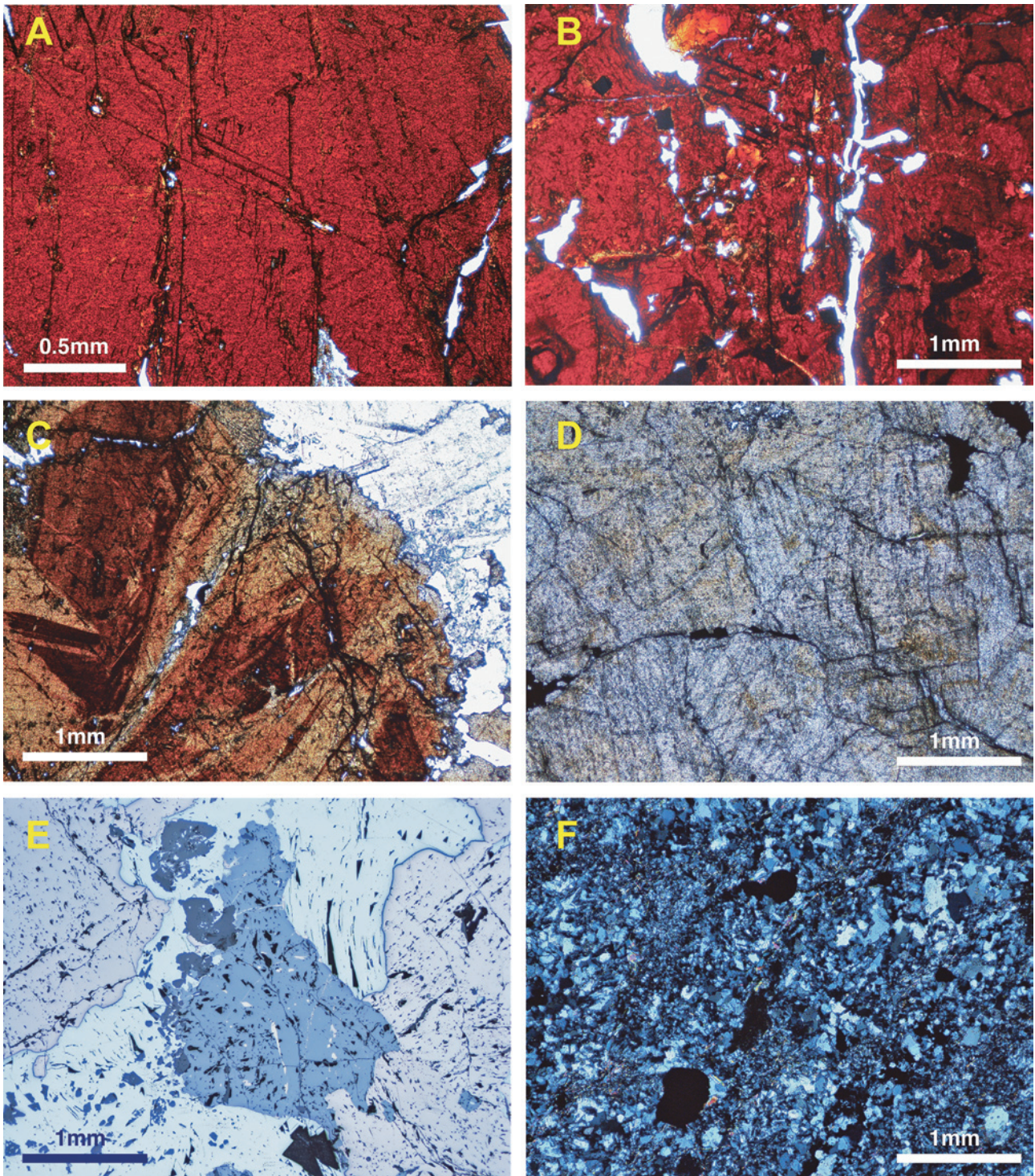


Plate II Microscopic pictures of selected minerals and rocks.

- A: Thin section color of homogeneous black sphalerite from the Na Tun mine. Single nicol.
- B: Thin section color of black sphalerite from the Na Bop mine (No.2). Single nicol.
- C: Thin section color of brown sphalerite from Cuo Duong mine. Note heterogeneous color variation. Single nicol.
- D: Pale brown sphalerite occurring with much carbonates from the Phudo mine. Note weak color variation. Single nicol.
- E: Galena (white) and sphalerite (dark grey) under reflective light. Dotted pyrrhotite inclusions occurring in the sphalerite (center). Na Bop mine (No. 2). Single nicol.
- F: Altered rhyolite; host rock for the Na Son mine (Na Son-36). Crossed nicols.

main constituents are galena and sphalerite, with minor amounts of magnetite, pyrrhotite, pyrite, arsenopyrite and chalcopyrite (Tinh ed., 2001). Our microscopic observation on a representative polished thin section indicates that the host rocks are recrystallized rhyolite (Plate IIF). The most common alteration minerals are sericite and lesser biotite with greenish brown on its Z color. Chlorite occurs very rarely as veinlet. Quartz and dolomite, both in vein form, are common. Fine grained aggregates of siderite and calcite are also observed.

Galena is much more dominant than sphalerite in this ore deposit. Galena is always anhedral form filling interstices of altered silicates, sphalerite and pyrite. The sphalerites are pale yellowish in color (low iron), containing chalcopyrite dots (i.e., chalcopyrite disease). Pyrite, often euhedral in form, is next common sulfide. Chalcopyrite occurs as small grains in anhedral form. Pyrrhotite is not present. Cerianite (CeTh)<sub>2</sub>O<sub>2</sub> was identified as a REE mineral.

## 2.2 Bac Kan region

Lead-zinc deposits are abundant in this region, as the Cho Dien mining field to the west (Fig. 3) including La Pointe, Deo An, Lung Hoai and many other small ones, and the Cho Don mining field to the southeast (Na Bop, Ba Bo, Na Tum and others; see the sheet map Bac Kan). Sy Binh ore deposit, described as Fe mine (Quoc ed., 2001) is located far east of Cho Dien, to the south of Nagson Sn-polymetallic mineralized region (Kiem and Luyen, 1991). Ore deposits of the Cho Dien field occur within the domed Cho Dien anticline (Fig. 3) of the Devonian clastic rocks with some impure limestone lenses at 5 to 12 km west of Cretaceous intrusive rocks (Quoc ed., 2001). The ore zones occur along NNE-fissure zones with steep dips in Lower Devonian, Pia Phuong Formation (D1pp1) of recrystallized limestone interbedded with some marl and sericite schist (450 m thick in total), and Upper Pia Phuong Formation (D1pp2) of thin-bedded sericite shale interbedded with sandy siltstone and black limestone lenses, 560-700 m thick in total.

In the Cho Don area to the south of Cho Dien, the host rocks are older, varying from Ordovician to Silurian, and are composed of sandstone, shale and impure limestone in the southeastern part, and Devonian in the northwestern part (Quoc ed., 2001). Syenitic rocks intrude into the sedimentary rocks in the middle of the mineralized area (Fig. 3). The Pb-Zn sulfides tend to occur in dolomitized and silicified carbonate rocks. Ore minerals fill up crushed host rocks and/or metasomatized into the host rocks. The mineralized zones have a NE-SW trend and dip nearly vertically, cross-cutting bedding plane of the host rocks. Apart from the anticline, the

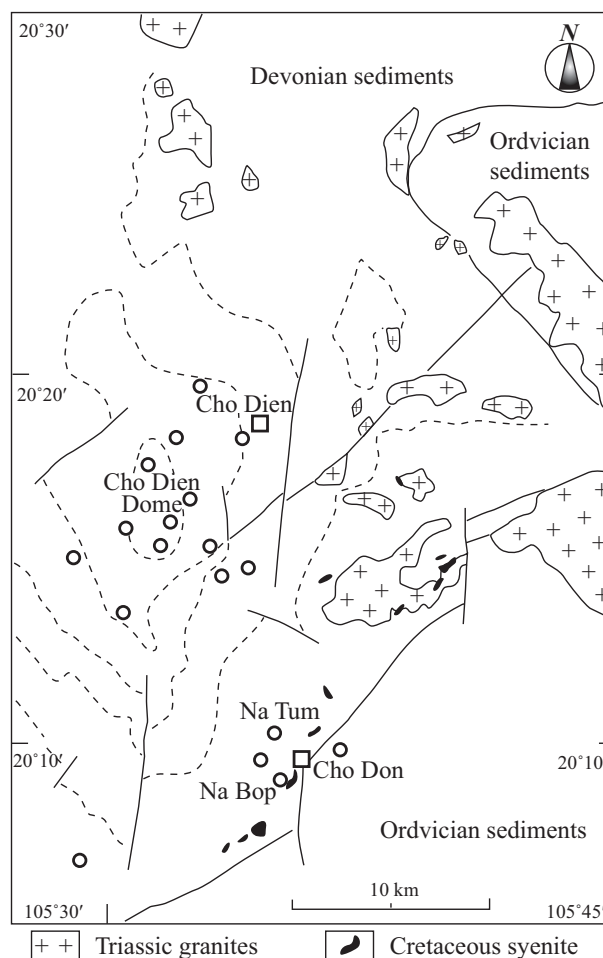


Fig. 3 Geological outline of the Cho Dien and Cho Don mining areas (simplified from Quoc, 2001).

mineralization locally follows the bedding plane of the host sedimentary rocks dipping 10-20°. The host rocks appear to be silt to fine sandstone in size. Sericite and calcite are most common alteration minerals.

Ore minerals of the Cho Don (Plate IB) and Cho Dien (Plates ID) areas occur mostly massive but partly foliated (Plate IC) in texture. They are composed of black to dark brown-colored sphalerite, pyrrhotite, galena, and rarely arsenopyrite, pyrite and chalcopyrite. Trace amounts of bismuthinite, argentite, wurtzite, stannite, melnikovite, tetrahedrite, tennantite, bourmonite and magnetite are also present with the gangue minerals of calcite and dolomite, with a little quartz, according to Quoc ed. (2001). Our microscopic studies on representative ores indicate that pyrrhotite is abundant and the sphalerite is reddish in color. Pyrite is also present. Pyrrhotite occurs as massive grains, and contains inclusion of sphalerite with chalcopyrite droplets. Galena is always later than these sulfides.

Sulfate minerals are said to occur in very trace amounts.

Upper parts of the lead-zinc ore bodies were oxidized to form the secondary ore bodies, which are composed of calamine, goethite and minor psilomelane, hydrogoethite, smithsonite, hydrozincite, cerussite and anglesite (Quoc ed., 2001).

### **2.3 Thai Nguyen region**

To the north of Thai Nguyen, several ore deposits have been known, including Phudo, Lang Hich (Mo Ba), Me Tic and Cuc Duong deposits (see Tuyen Quang sheet by Long ed., 2001). This region is underlain by Cambrian to Carboniferous clastic and carbonate rocks. The largest Lang Hich deposits occur along the Than Sa anticline of Devonian Song Cau Group of basal conglomerate, quartz sandstone, chocolate siltstone, shale and dolomitic limestone (Long ed., 2001). Unique Cuc Duong deposit occurs in Triassic Song Hien Formation, composed of thick bedded limestone. The mineralization is distributed in crushed zone of carbonate rocks. One unit of the ore deposits is composed of several high-grade parts which extends 25-300 m along the strike, 1-4 m in the width, and 100 m deep. The ore reserves could vary from 10 to 50 thousand tons (Long ed., 2001).

The main ore minerals are composed of galena, sphalerite and pyrite. The Pb-Zn grade may be 2 to 25 % (Long ed., 2001). The sphalerite is pale brown in color occurring with much carbonates in the Phudo ores (Plate IE). In the Lang Hich deposit, iron sulfides are small in amount, but a moderate in the Me Tic deposit, and much more abundant in the Cuc Duong deposit. The Cuc Duong ores are unique containing rhodochrosite with brownish staining as most common gangue mineral (Plate IF), which was determined by x-ray diffraction.

The upper part of each ore deposit has been oxidized to secondary ores, consisting of cerussite, anglesite, smithsonite and calamine. These secondary ores are also economically important (Long ed., 2001).

## **3. Analytical results of studied Pb-Zn ores**

Microphotographs of selected ores are shown in Plate II. Their host rocks are sedimentary rocks, except for the Na Son ores (Plate IA). Color of sphalerites varies from dark red to colorless under the transparent microscope (Plate IIA-D). The analytical results are shown in Appendices 1 to 3.

It is obvious from these tables that the Na Son type ores are unique having high contents of Mo, REE and Y, K and Rb, and Th and U, which are generally concentrated in highly fractionated in ilmenite-series granitic and hydrothermal activities (Ishihara and Murakami, 2006). Besides, we have galena and sphalerite mineralization here. It is therefore

interesting to know of redox status of the rhyolite. The Na Son ores contain muscovite and biotite as alteration minerals, thus they appear to be higher temperature than the other ore deposits. Therefore, the Pb-Zn mineralization may be related to hydrothermal activities of the host rhyolitic and/or nearby intrusive rocks if any.

The sediments-hosted ore deposits have variable amounts of Ca, which seems originated in recrystallized carbonates of the host rocks. For example, ores of the Na Bop deposits and Cho Dien deposits contain 0.1 – 20.6 % Ca (n=10) and 0.03 – 30.3 % Ca (n=15), respectively. Ores of the Lang Hich deposits have 0.4 to 29.3 % Ca (n=13). Both the Me Tic and Cuc Duong deposits are low in Ca as 0.4 to 6.1 % (n=5) and 0.7 to 4.9 % (n=6), respectively. The Cuc Duong deposits are high in manganese (3.4 to 9.8 % Mn) and iron (7.9 – 17.9 % Fe, n=6). The contained carbonate is not pink but brownish white, which is determined to be rhodochrosite by x-ray diffraction and microscopic identifications.

Ores of the Na Bop deposits contain 10.3 to 38.4 % Fe, except for two low values of 2.0 and 3.5 % Fe. Those of Cho Dien deposits are also high in iron as 7.2 – 37.0 % Fe, except for 3.8 % Fe value. These high Fe values are caused by Fe-rich sphalerites (Plates IIA, B) and pyrrhotite and pyrite contained. All the sediments-hosted ores are low in REE and Y, and Th and U.

### **3.1 Variations in major ore components**

The studied Pb-Zn ores have a wide variation in the Fe content. The studied ores are primary ores and contain reddish hematite. A high magnetic susceptibility of  $28.5 \times 10^{-3}$  SI unit was observed on Cho Dien-1616 samples, which is solely composed of Fe-bearing minerals, such as magnetite, pyrrhotite, pyrite and arsenopyrite.

Iron and manganese contents vary widely. The ores of Cuc Duong deposits are richest in Mn contents (Appendix 1) and Mn/Fe ratio (Fig. 4A), which are due to contained rhodochrosite. The next group of the ores having Fe/Mn ratio between 10 and 100 are those of Cho Dien, Na Son and Lang Hich, but the absolute amounts of Fe are quite different; highest in the Cho Dien ores, then the Na Son ores, and the Lang Hich ores. The Na Bop ores have higher Fe/Mn ratio than the Cho Dien ores. The Phudo ores are most depleted in iron and manganese (Fig. 4A).

Besides iron oxide and sulfides, sphalerites can contain appreciable amounts of iron. Pale color sphalerite contained in the ores from the Phudo deposit are plotted in the left-bottom corner of Fig. 4A. High Zn grade ores from the Lang Hich and Me Tic deposits are plotted in similar area, implying these are composed of low-Fe sphalerites. No clear

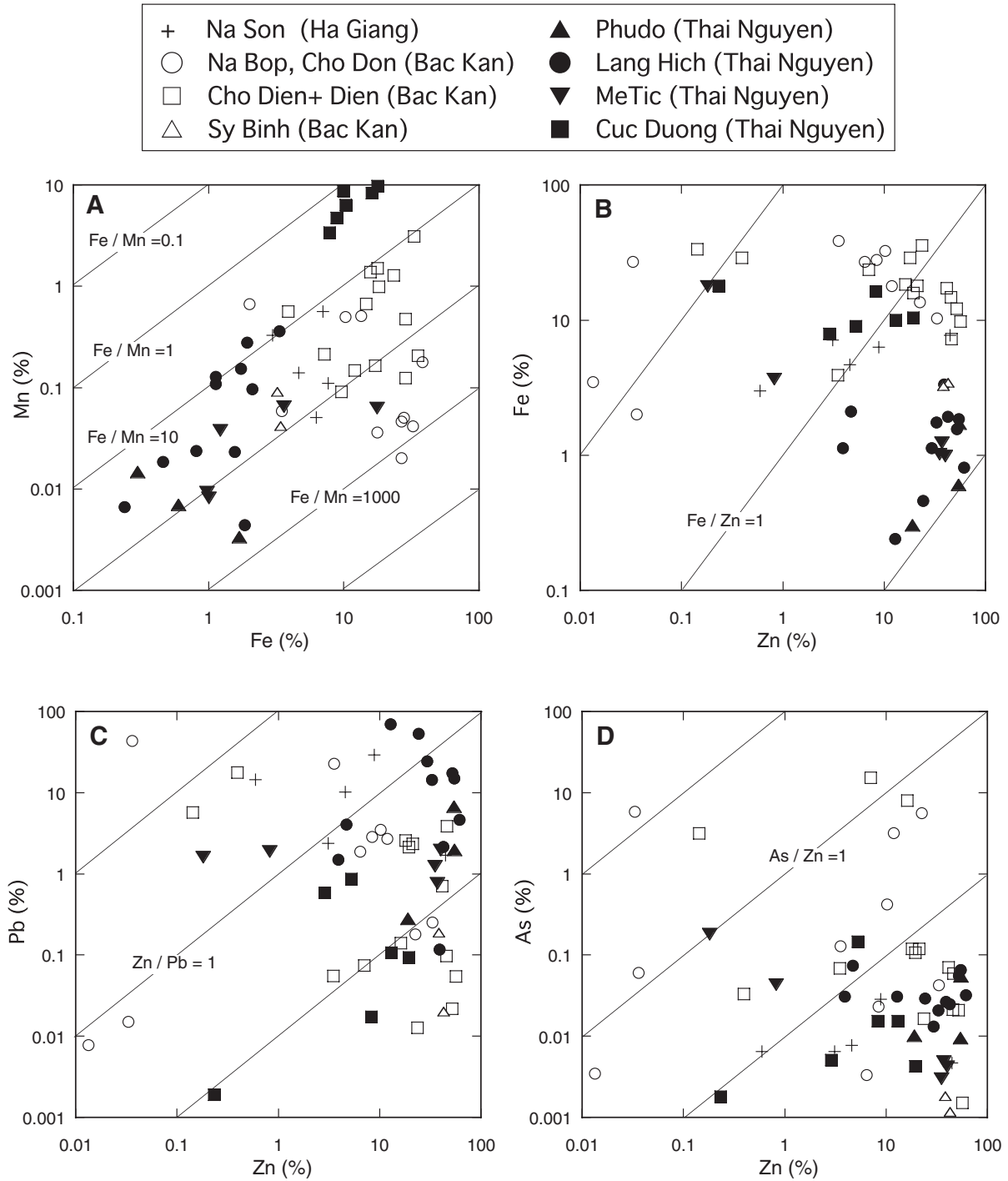


Fig. 4 Binary diagrams for Mn-Fe, Fe-Zn, Pb-Zn and As-Zn of the studied Pb-Zn ores.

positive correlation observed on Fe vs. Zn diagram (Fig. 4B); some ores have the Fe/Zn ratio higher than 0.5, which indicates that Fe-sulfides are dominant source for the iron of the ores. Ores from the Na Bop and Cho Dien deposits are plotted in the most iron-rich area (Fig. 4B), while those of the Cuc Duong deposits are less in iron than the ores of these two ore deposits, and those of the MeTic and Lang Hich are

least in the Fe/Zn ratio (Fig. 4B).

Pb/Zn ratios of the studied ores are generally below the unity, but the Na Son ores have the ratio higher than unity (Fig. 4C). The ores from the Cuc Duong and Phudo deposits and a part of Cho Dien deposits have the highest Zn/Pb ratio. Arsenic seems to have no correlation with Zn contents of the ores. Its contents are generally less than 1,000 ppm As, but

up to 15 % As, in some ores of the Na Bop and Cho Dien deposits (Fig. 4D). Arsenic is very poorly correlated with the bulk Fe contents.

### 3.2 Variation in minor ore components

Trace amounts of In tend to occur in tin-polymetallic base-metal deposits (Ishihara *et al.*, 2006). Here, a positive correlation is observed between In and Sn contents excluding

the Cuc Duong ores (Fig. 5A), due to the high contents of the Pb-Zn ores in the Bac Kan region and low contents of the Pb-Zn ores in the Thai Nguyen region, with the Na Son ores in-between. The highest In contents were observed in those of the Na Bop mine. Although indium is considered to occur in sphalerite (Ishihara *et al.*, 2006; Ishihara and Endo, 2007), a positive correlation in the In-Zn diagram is not clear (Fig. 5B), because of low In-values on the Lang Hich, Me Tic and

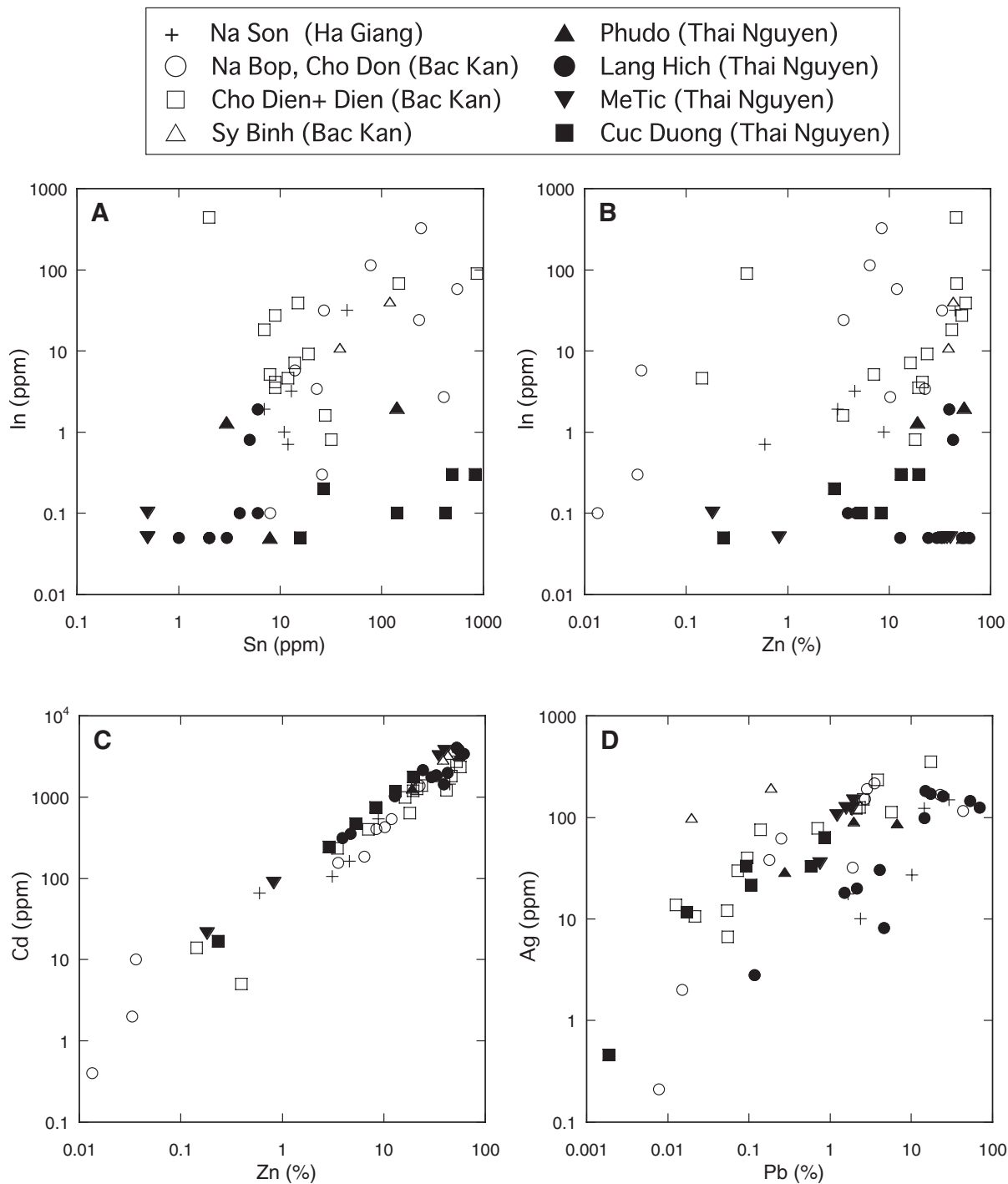


Fig. 5 Binary diagrams for In-Sn, In-Zn, Cd-Zn and Ag-Pb of the studied Pb-Zn ores.



Cuc Duong ores, which occur purely sedimentary terrains.

Cadmium is exclusively contained in sphalerite and the best positive correlation has been observed here (Fig. 5C) and everywhere (e.g., Ishihara *et al.*, 2006). In details, ores from the Na Son, Na Bop and Cho Dien deposits have lower Cd/Zn ratios than other deposits, as shown in Fig. 5C and also in Appendix 1, which indicates that sphalerites from these deposits have lower Cd concentration than that from

other deposits. Amounts of silver are positively correlated with those of lead (Fig. 5D). Ag/Pb ratio seems highest in Pb-Zn ores from the Bac Kan region (Fig. 5D).

Bismuth is generally rich in the ores from the Bac Kan region, while it is poor in those of the Thai Nguyen and Ha Giang regions (Fig. 6A). Antimony and Ag, which may be precipitated in low temperature conditions, have good positive correlations in most of the ore deposits in the Thai

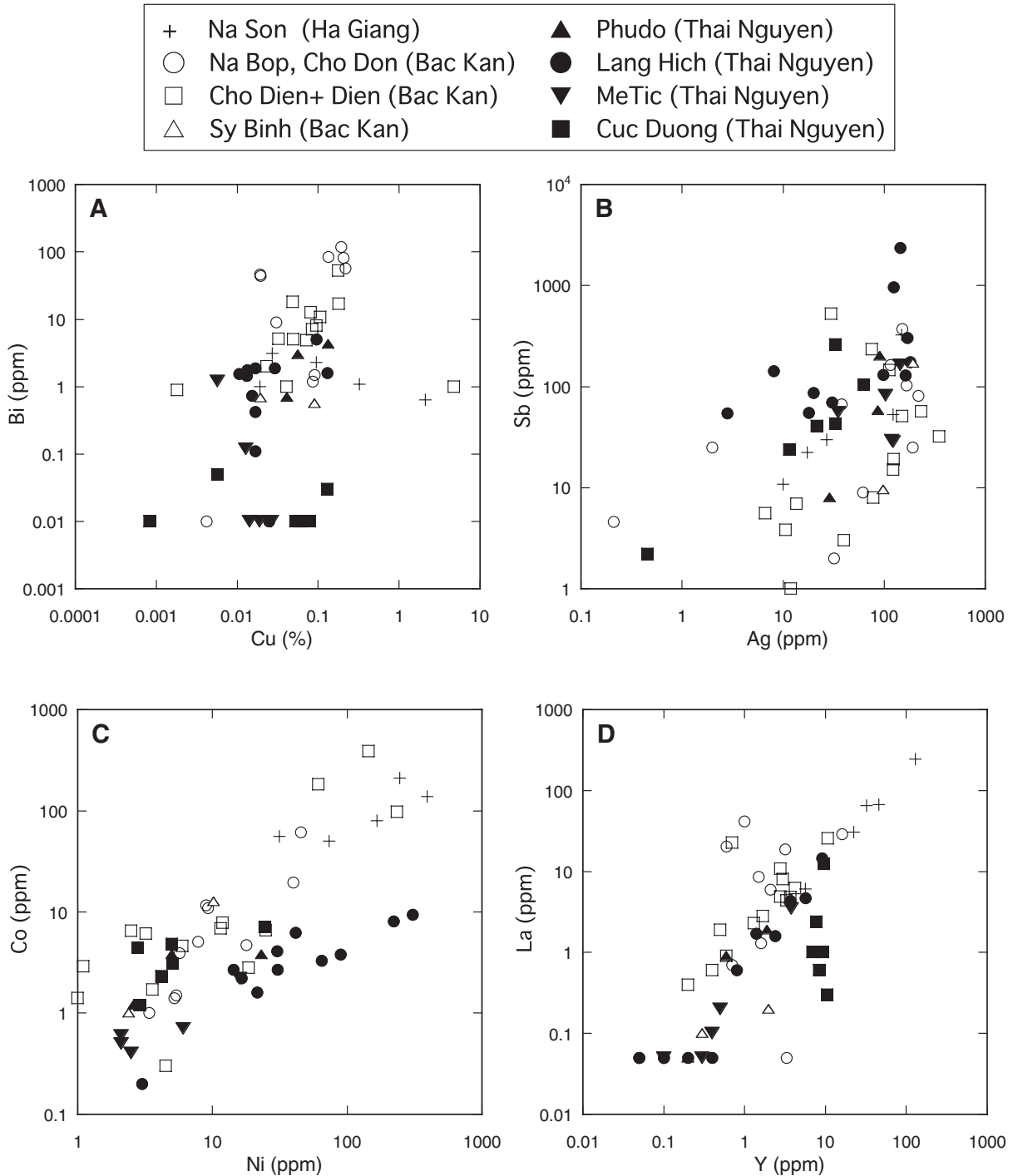


Fig. 6 Binary diagrams for Bi-Cu, Sb-Ag, Co-Ni and La-Y of the studied Pb-Zn ores.

Nguyen province (Fig. 6B). Cobalt and Ni show a good positive correlation. Their contents are high in the ores from the Na Son, Cho Dien and Na Bop deposits. Ores of the Lang Hich deposits are unique having high Ni/Co ratio (Fig. 6C).

Mo contents are outstanding in the Pb-Zn ores from the Na Son mine, and Co and Cu contents are also high in the ore deposits (Appendix 1). It is rather strange to have high concentration of La and Y in the Pb-Zn ores. These contents are generally high in those of the Na Son mine, then of the Bac Kan region, and the lowest in those of the Thai Nguyen region (Fig. 6D). High concentration of REE in the Na Son deposit must be connected with the rock series and its degree of fractionation of the host rhyolites.

### 3.3 REE contents and REE patterns

In the northern Vietnam, base metal deposits are associated with REE minerals. In Sin Quyen IOCG deposits (McLean, 2001), the main mineralization occur in three stages as,

Stage I: magnetite-allanite-pyrrhotite-pyrite occurring in metasomatite and skarn bodies,

Stage II: chalcopyrite-pyrite-pyrrhotite-sphalerite-cubanite-valleriite, and

Stage III: quartz-calcite-pyrite-marcasite of low temperature formation.

Allanite and other REE minerals occur usually filling fractures of Stages I and II minerals (McLean, 2001).

In the Na Son deposits, the most distinct REE-mineral is cerianite (Ce) as determined by x-ray diffraction by Dr. M. Hoshino, AIST. Its REE pattern is therefore rich in LREE as shown in Fig. 7. The highest and second highest REE rocks of Na Son-36 (1,210 ppm) and 38 (842 ppm, Appendix 3) are shown in the figure. Both show similar pattern to those of igneous rocks, and No. 36 sample has strongest Eu-negative anomaly, implying that the mineralization was associated with the host rhyolite which had a strong plagioclase fractionation at the magmatic stage of the ore fluid. The second highest, Na Tum sample (842 ppm, Appendix 3), has similar REE pattern, but depleted highly in the HREE. There is also a weak Ce-negative anomaly observable, which indicates oxidation of the ore fluids just before precipitation of the REE minerals.

## 4. Classification of the Pb-Zn deposits

### 4.1 Previous results

Tran *et al.* (2009) classified these ore deposits into three major types, as follows:

(1) Sphalerite-galena-pyrite or galena-sphalerite mineralization in terrigenous carbonate rocks, concentrated in Cho Dien,

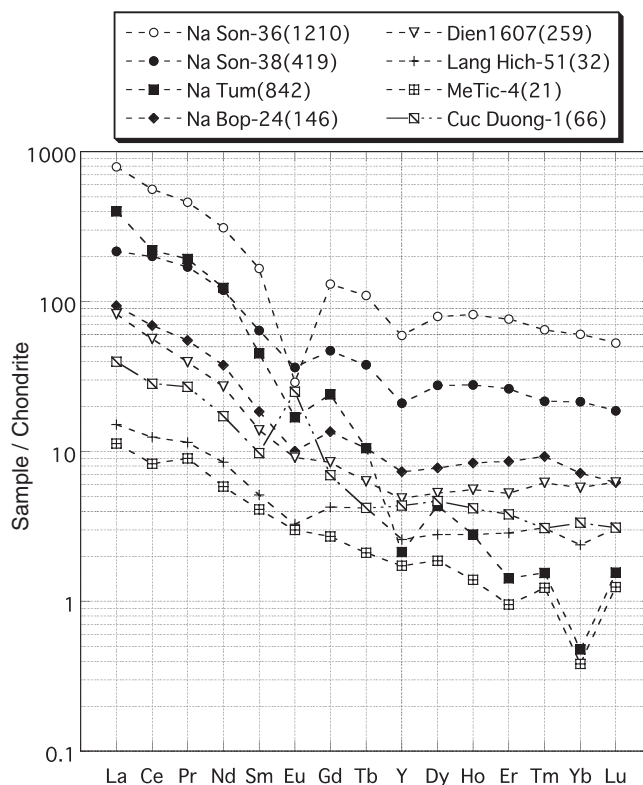


Fig. 7 REE patterns of representative Pb-Zn ores from northern Vietnam.

Cho Don (Bac Kan) and Lang Hich (Thai Nguyen) ore fields. Therefore, it can be called sediments hosted type. This group of ores are most studied in this paper, and the ores are subdivided into several sub types on the basis of their chemical characteristics.

- (2) Chalcopyrite-galena-sphalerite or galena-sphalerite occurring in volcanic-sedimentary rocks, located along the Song Da and Tu Le structures in the northwestern region. The major one is seen in the Na Son deposits in alkaline rhyolites as galena-sphalerite-chalcopyrite-pyrrhotite ores. This could be called Na Son sub type, which is related to rhyolitic activity.
- (3) Pb-Zn ores in association with intrusive rocks, consisting of polymetallic-tin mineralization (Ngan Son type), which can be called intrusion-related type. No ores were available from this group of ore deposits in this study.

On the first type of the lead-zinc deposits occurring often in carbonate rocks, there is a proposal that many or all of these deposits could be Mississippi Valley type (e.g., Watanabe, 2000; Kohno *et al.*, 2008). MVT deposits were named after lead-zinc ore deposits in the central part of Mississippi Valley, U. S. A., for those having the following characteristics (Ishihara, 1985):

- (i) The ores occur in Paleozoic carbonate rocks and rarely shale and sandstone, with stratigraphic controls in a broad sense, but the ores are directly hosted in dissolved breccia, paleo-karst, and reef.
- (ii) The ore minerals are mostly sphalerite and galena, accompanying barite, fluorite, pyrite and marcasite.
- (iii) Wall rock alteration is usually dolomitization,
- (iv) The sphalerites are pale in color and contains low-temperature (160-70 °C) fluid inclusions with high salinity.
- (v) Sulfur isotopes are generally heavy, and Pb isotopes are abnormal indicating either younger or older ages than the host rocks.

The carbonate hosted Pb-Zn deposits studied here are controlled by local faults and bedding plane of the host rocks. Yet the mineralization is not controlled by dissolved breccia and paleo-karst.

MVT ores usually have very low contents of Fe (300~20,000 ppm) but high contents of Cd (3,000 ~15,000 ppm) in the sphalerite (Viets *et al.*, 1992), or Cd 390 ~50,000 ppm with a mean of 4,850 ppm in the bulk ore samples (Schwartz, 2000). High In-sphalerite and pyrrhotite cannot be concentrated in MVT ores, because these minerals occur in a high-temperature environment of hydrothermal system (Ohta, 1995). Trace amounts of tin discovered in some ores from the first-type of the ore deposits are also unusual for the MVT ore deposits.

The In-Sn rich sphalerite deposits of Dulong mine in the Chinese side (Fig. 1) are spatially and genetically related to muscovite-biotite granite of Yanshanian age. The largest In-bearing ore deposits of the Dachang, Kwangxi Province, are also genetically connected with the Yanshanian felsic intrusives (Ishihara *et al.*, 2008). No samples were obtained from similar ore deposits of the Ngan Son type in this study, but it is very interesting to know of chemical characteristics of the Pb-Zn ores occurring in the Ngan Son area.

#### 4.2 Present Results

The studied Pb-Zn ores show a variety of chemical compositions and are therefore classified into four subtypes as follows:

- (1) REE-rich Pb=Zn subtype, e. g., Na Son, REE up to 1,210 ppm (avg. Fe 5.7%)
- (2) In-Fe-rich Zn>Pb subtype; e.g., Na Bop (avg. Fe 20.0 %), Na Tum (avg. Fe 16.0 %) and Cho Dien (avg. Fe 19.1%).
- (3) In-Fe-poor Zn>Pb subtype, e.g., Lang Hich (avg. Fe 1.4 %), Me Tic (avg. Fe 4.9 %); and Phudo (avg. Fe=0.87).
- (4) Mn-Fe-rich Zn>Pb subtype, Cuc Duong (avg. Mn 6.9 %; avg. Fe 11.9 %)

The Na Son subtype is relatively rich in lead and shows an igneous REE pattern. Therefore, the mineralization is considered genetically related to the host rhyolitic rocks. Many ore deposits in the Cho Don and Cho Dien areas are characterized by the Pb-Zn ores with abundant pyrrhotite, magnetite, pyrite and Fe-rich black sphalerites, and In anomalies were discovered locally. Although the studied ores of the Na Bop and Cho Dien mines revealed similar high Fe contents as 20.0 % for the Na Bop mine and 19.1 % for the Cho Dien mine, Zn concentrates values are 23.2 % Fe vs. 7.73 % Fe, respectively, however. This fact implies that the Na Bop sphalerites are three times Fe-rich than the Cho Dien sphalerites, because the Fe sulfides have been moved out in the Zn concentrates. Indium is hosted usually in Fe-rich sphalerite at Toyoha mine (Ohta, 1995) and everywhere (Ishihara *et al.*, 2006).

Near the Na Bop mine of Cho Don area, syenitic dikes are described in the middle of Pb-Zn mineralized area (Fig. 2). Biotite hornfels is clearly observed in the drill cores of the Na Bop mine. Indium is best concentrated in Sn-bearing hypothermal ore fluids liberated from ilmenite-series granitic magmas in southern China (Ishihara and Murakami, 2008) and Bolivia (Ishihara and Murakami, 2007). The highest In-concentration is observed at the conduit of hypothermal ore fluids at Toyoha mine (Ohta, 1995). Some parts of the ore fluids in the Cho Don and Cho Dien region appear to be reduced and derived from hidden ilmenite-series granitic intrusion.

On the contrary, the Pb-Zn ores from Lang Hich mine region are very depleted in Fe and In. The Me Tic ores would belong to the same group but higher in iron (avg. 4.9 % Fe), and have the highest in (Cd/Zn) x 10<sup>3</sup> ratio of 8.7. Chemically speaking, these two ore deposits may be closest to MVT ores. The Cuc Duong ores are also unique having high content of iron (avg. 11.9 % Fe) and manganese (avg. 6.9% Mn) and also trace amounts of tin (avg. 325 ppm Sn). In the Malay Peninsula region, cassiterite is mainly concentrated with a hypothermal ore fluid rather than a mesothermal one (e.g., Kosaba deposit, Ishihara *et al.*, 1980), we should study further details of these Pb-Zn ores.

#### 5. Indium contents of Zn-ores and Zn-concentrates

As mentioned previously, the present chemical analyses show sporadic In-anomalies in the Cho Don and Cho Dien ores. The highest anomaly is found in those of Na Bop mine of the Cho Don area, as 329 ppm for 8.5 % Zn ore. If this content were normalized to idealized ZnS with 67.1 % Zn, a calculated In-value of 2603 ppm is obtained, which is here

Table 1 Averaged selected parameters on the Pb-Zn ores from the northern Vietnam.

Ore deposits	In	Zn %	In-sp	Sn	Cd	Cd-sp	(Cd/Zn)x10 <sup>3</sup>	Fe%
<i>Averages of ores</i>								
Na Son (n=5)	7.7	12.5	41	17.8	465	2511	3.7	5.7
Sy Binh (n=2)	25.7	41.2	42	80	3085	5029	7.5	3.3
Na Bop (n=7)	80.4	13.8	665	225	702	3415	5.1	20.0
Cho Dien (n=13)	48.4	27.2	243	24	1299	4404	4.4	19.1
Phudo (n=3)	1.1	43.3	1.7	51	2827	4381	6.5	0.9
Lang Hich (n=11)	0.3	32.7	0.5	3.1	2028	4157	6.2	1.4
Me Tic (n=5)	<0.1	22.9	<1	<1	1996	5853	8.7	4.9
Cuc Duong (n=5)	0.2	8.3	1.6	325	699	5669	8.5	11.9
<i>Zn concentrates</i>								
Na Son (n=1)	3.8	15.3	16.7	11	1090	4780	7.1	4.7
Na Bop (n=1)	698	36.6	1280	416	1550	2842	4.2	23.2
Cho Dien (n=1)	228	49.8	307	54	2640	3557	5.3	7.7
Land Hich (n=1)	0.8	57.8	0.9	11	4130	4795	7.2	1.1

The unit is ppm excluding Zn and Fe.

considered as In content in sphalerite (In-sp) and listed in the Table 1. In this calculation, Zn contents less than 5,000 ppm were excluded because of large errors expected. In the most In-enriched Na Bop deposits, this value ranges from 10 ppm to 2,603 ppm and averaged as 665 ppm. The Cho Dien deposits have the value between 3 and 2,144 ppm with an average of 243 ppm (Table 1).

In-bearing Zn concentrates are a major source for indium extraction in the industrial use and recent sharp increasing of the price and demand made the contents in zinc deposits attractive throughout the world (Ishihara, 2005). The highest In-grade among Zn-concentrates was obtained from Toyoha mine. Its 2005 concentrates contained 1,030~1,230 ppm In at 56.6% Zn (Ishihara *et al.*, 2006), whose In-sp values are 1,221 to 1,458 ppm. Zinc concentrates of the Brunswick mine, which is one of major In producers in this world, contain 215 to 254 ppm In around the same year (Ishihara and Murakami, 2007). Preliminary results of the studied ore deposits are shown in Table 1.

The Zn concentrates of 2008 year from the Na Bop mine contain 698 ppm In for 36.6 % Zn. Therefore, its In-sp value is 1280 ppm In, which is similar to the high values of the Toyoha mine. However, this is much higher than the averaged In-sp value (391 ppm In) of 7 ore samples from the Na Bop mine. Therefore, we need more work on the Pb-Zn ores from the Na Bop mine. The Zn concentrates of 2008 year from the Cho Dien mine contain 228 ppm for 49.8 % Zn, which gives 307 ppm In-sp value. These two deposits have economic value on the indium contents. Zinc concentrates from the Na

Son deposits and Lang Hich deposits are lower than 16.7 ppm In-sp, and have no commercial values.

## 6. Conclusions

Pb-Zn ores in the northern Vietnam occur in Paleozoic sedimentary rocks containing abundant impure limestone, and also in Triassic rhyolite. They are chemically subdivided into several subtypes, based upon their REE content, Fe and Mn contents and ratio, and others. Although some proposed MVT geneses for these ore deposits, the Pb-Zn ores contain very high iron in the ores and also in sphalerite, and low in Cd. Most of the ore deposits seem to have been formed by epigenetic circulation of hydrothermal fluids liberated from felsic igneous activities in the deformed and sheared host rocks. Iron-rich sphalerites of the Na Bop mine are considered occurring closest to “ore-bringer” of granitic and/or syenitic compositions, and have economically an important level of indium concentration. Yet further study is necessary systematically for the Zn concentrates from this mine.

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## 北部ベトナム産の鉛亜鉛鉱石の化学的特徴, 特にインジウム含有量について

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### 要 旨

インジウムに富む閃亜鉛鉱を探す目的で、ベトナム最北部の古生代堆積岩類に胚胎する鉛亜鉛鉱石を分析した。ここではインジウム (In) 異常と共に、これら鉱床をミシシッピーバレー型とする見解も提案されている。今回の研究の結果、鉱床は下記のような多種類に亘ることが判明した。(1) REE に富む(最大 1210 ppm) 鉛-亜鉛鉱床 (Na Som)。これは流紋岩と関係し、変質鉱物から高温熱水性と考えられる。(2) In と Fe に富む亜鉛>鉛-磁硫鉄鉱床 (Na Bop)。これは還元的な高温熱水性である。(3) In と Fe に乏しい閃亜鉛鉱>方鉛鉱床 (Lang Hich, Mi Tic, Phudo), (4) Mn 炭酸塩に富む鉄閃亜鉛鉱>方鉛鉱床 (Cuc Duong)。上記2者は低温熱水性である。

Bac Kan 地区では Na Bop 鉱床の鉛亜鉛鉱石からは、経済性を持つ In 異常が発見され、Cho Dien 鉱床からは弱い In 異常が発見された。これら鉱石は花崗岩質岩脈に近い鉱床で産し、鉄に富む黒色閃亜鉛鉱と磁硫鉄鉱を多く含み、還元的な高温熱水性環境下の生成である。Cho Dien では多数の鉛亜鉛鉱床が発見されており、それらは Cho Dien ドーム構造を持つ古生層中に胚胎する。ドームの下部には珪長質貫入岩が潜在するものと思われ、その結果として多くの鉱床がここに生成されたものと考えられる。貫入岩はチタン鉄鉱系のスズ花崗岩であり、花崗岩に近い鉱床にインジウムは濃集した可能性が大きい。鉱石の閃亜鉛鉱中のインジウム最高値  $In_{sp}=391$  及び Na Bop 鉱山の亜鉛精鉱中の 898 ppm In は、共にインジウムが経済性を持つことを示唆している。

Chemical characteristics of lead-zinc ores (Ishihara et al.)

Appendix 1 Analytical result of In to Fe-Mn of the Pb-Zn ores from northern Vietnam.

Appendix-1

Analyte Symbol Detection Limit	In 0.1	In-sp	Sn 1	Cd 0.1	Zn 0.2	Pb 1	Cu 0	As 0.1	Co 0.1	Ni 0.5	Bi 0.02	Mo 0.1	Ag 0.05	Sb 0.1	Se 0.1	Fe (%) 0.01	Mn 1
<b>Ha Giang Province</b>																	
Na Son-14	1.9	41	7	105	31400	23700	192	65	79.4	167.0	1.0	15.2	10.0	10.8	1.7	7.06	5620
Na Son-35	3.2	47	13	163	46200	102000	273	77	138.0	395.0	3.1	29.0	27.1	29.6	2.3	4.66	1390
Na Son-36	0.7	79.0	12	66	5980	145000	3290	64	55.7	31.6	1.1	257.0	123.0	53.0	2.6	2.99	3270
Na Son-37	31.5	47.0	46	1450	450000	16900	961	47	50.2	73.6	2.3	18.0	17.5	22.2	9.8	7.72	1100
Na Son-38	1.0	8.0	11	539	89300	292000	21400	281	211.0	247.0	0.6	3870	149.0	323.0	2.7	6.28	503
<b>Bac Kan Province</b>																	
Sy Binh-1a	40.4	40.0	121	3300	434000	198	194	12	2.4	1.0	0.7	0.7	98.6	9.6	21.9	3.42	415
Sy Binh-1d	10.9	19.0	39	2870	389000	1870	910	18	10.2	12.7	0.6	1.2	194.0	170.0	19.8	3.23	901
Ba Bo, Cho Don	4.9	n.c.	40	6	386	192000	60	1620	6.8	14.8	< 0.02	0.9	144.0	72.4	0.6	19.60	7880
Na Tum, Cho Don	84.0	527.0	743	339	107000	312000	1310	60700	2.5	7.4	386.0	1.0	154.0	354.0	3.3	16.00	13100
Na Bop-3, ditto	5.8	n.c.	14	10	363	434000	191	602	1.4	5.2	46.1	0.3	116.0	163.0	3.8	2.01	6680
Na Bop-4, ditto	24.1	452.0	235	156	35800	228000	303	1290	1.5	5.4	9.0	0.3	167.0	103.0	1.5	38.40	1780
Na Bop-24, ditto	0.1	n.c.	8	0	134	78	42	34	19.5	40.0	< 0.02	2.7	0.2	4.6	1.1	3.49	585
Na Bop1610, ditto	114.0	1184.0	78	187	64600	18900	909	33	3.9	5.7	1.5	0.5	32.0	2.0	<0.1	26.90	465
Na Bop1611, ditto	2.7	18.0	411	427	103000	35100	859	4190	11.6	9.0	1.2	0.4	218.0	81.0	<0.1	32.60	417
Na Bop1612, ditto	329.0	2603.0	245	404	84800	28400	2070	231	5.1	7.8	81.0	0.3	191.0	25.0	3.2	27.90	507
Na Bop1613, ditto	58.3	326.0	557	539	120000	26900	1930	32000	1.0	3.4	119.0	0.5	152.0	374.0	5.0	17.80	362
Na Bop1614, ditto	3.4	10.0	23	1390	225000	1790	194	56400	10.9	9.3	44.0	0.3	38.0	67.0	8.6	13.50	5090
Na Bop1615, ditto	31.6	64.0	27	1810	332000	2510	2170	427	4.7	17.8	57.0	0.2	62.0	9.0	12.4	10.30	4960
Na Bop1616, ditto	0.3	n.c.	26	2	330	150	1340	58500	61.4	45.3	84.0	1.0	2.0	25.0	<0.1	26.90	202
Cho Dien 1601	4.1	13.0	9	1260	214000	23200	960	1180	7.8	11.9	8.0	0.9	125.0	19.0	8.2	17.90	14900
Cho Dien 1602A	3.5	12.0	9	1190	196000	21200	850	1070	6.9	11.5	7.0	0.9	123.0	15.0	7.1	15.80	13700
Cho Dien1602B	18.3	29.0	7	1210	420000	7020	1790	700	2.9	1.1	53.0	0.3	78.0	8.0	<0.1	17.20	1630
Cho Dien 1603	0.8	3.0	32	631	182000	25700	411	1190	6.1	3.2	1.0	0.8	151.0	51.0	<0.1	28.80	1230
Cho Dien1604	442.0	646.0	2	1400	459000	960	494	210	2.8	18.6	5.0	2.0	40.0	3.0	<0.1	14.70	6640
Cho Dien1605	38.6	46.0	15	2340	569000	540	233	15	1.4	1.0	2.0	0.3	12.0	1.0	<0.1	9.70	907
Cho Dien 1607	89.0	n.c.	869	5	3980	176000	47600	329	97.4	235.0	1.0	1.2	353.0	32.0	0.8	28.90	4710
Cho Dien1608	67.0	96.0	148	1810	467000	38500	1810	589	4.6	6.0	17.0	2.6	234.0	57.0	<0.1	7.20	2110
Cho Dien-5	9.2	26.0	19	1380	238000	127	819	162	1.7	3.6	12.6	1.0	13.7	6.9	4.9	35.50	2060
Cho Dien-6	5.1	48.0	8	403	71100	733	491	152000	387.0	144.0	18.1	0.7	29.9	527.0	3.5	23.60	12700
Cho Dien-7	1.6	31.0	28	232	35100	550	18	685	6.6	25.0	0.9	3.9	6.7	5.6	1.5	3.90	5590
Cho Dien-8	4.6	2144.0	12	14	1440	57000	723	31300	0.3	4.5	4.9	1.9	113.0	145.0	1.2	33.40	30800
Cho Dien-26	27.4	35.0	9	2740	525000	216	323	209	6.5	2.5	5.1	1.7	10.6	3.8	11.1	12.10	1470
Cho Dien-27	7.1	29.0	14	994	164000	1400	1060	79300	183.0	61.2	10.8	0.7	75.6	234.0	4.4	18.30	9840
<b>Thai Nguyen Province</b>																	
Phudo1617	2.0	2.4	143	3180	556000	19700	1340	540	3.8	23.2	4.3	0.5	91.0	200.0	<0.1	1.70	33
Phudo1618	<0.1	0.1	8	4040	550000	67000	414	93	1.2	2.6	0.7	0.3	87.0	58.0	<0.1	0.60	69
Phudo 1619	1.3	4.5	3	1260	193000	2770	562	100	3.8	5.0	3.0	<0.1	29.0	8.0		0.30	145
Lang Hieh-9	< 0.1	<0.1	2	4070	526000	173000	133	553	1.6	21.5	1.8	1.4	171.0	303.0	10.6	1.56	231
Lang Hieh-10	< 0.1	<0.3	2	2160	245000	531000	964	291	9.4	306.0	5.1	0.5	145.0	2350.0	5.1	0.46	185
Lang Hieh-11	< 0.1	<0.1	3	3430	616000	46200	167	319	0.2	3.0	1.9	0.5	8.1	142.0	13.1	0.81	237
Lang Hieh-12	1.9	3.3	6	1450	392000	1170	153	264	3.3	64.8	0.7	0.7	2.8	54.2	7.9	3.34	3610
Lang Hieh-13	< 0.1	<0.2	2	1860	330000	145000	250	207	4.1	30.3	< 0.02	1.1	98.4	130.0	6.4	1.74	1530
Lang Hieh-30	< 0.1	<0.1	1	3880	548000	150000	131	653	2.7	30.6	1.4	1.1	183.0	174.0	11.3	1.85	44
Lang Hieh-31	< 0.1	<0.5	1	1030	129000	695000	1300	308	8.1	222.0	1.6	0.1	125.0	965.0	2.7	0.24	66
Lang Hieh-33	0.8	1.3	5	1990	425000	21400	168	247	3.8	89.9	0.4	0.8	20.0	86.4	9.3	1.93	2770
Lang Hieh-34	< 0.1	<0.2	2	1770	297000	245000	167	132	2.7	14.3	0.1	0.9	163.0	129.0	6.1	1.13	1270
Lang Hieh-51	0.1	1.7	4	313	39400	15000	106	309	2.2	16.5	1.5	0.8	18.1	55.2	1.8	1.13	1080
Lang Hieh-52	0.1	1.4	6	354	47000	40700	293	734	6.2	41.5	1.9	2.5	30.5	69.6	3.5	2.11	963
MeTic-1	< 0.1	<8.1	< 1	88	8250	18800	128	433	0.7	6.1	0.1	1.3	120.0	29.5	1.2	3.64	648
MeTic-2	< 0.1	<0.2	< 1	3680	405000	19600	264	42	0.5	2.1	< 0.02	0.1	145.0	163.0	19.7	0.98	93
MeTic-3	0.1	n.c.	< 1	21	1820	16000	57	1790	2.2	16.0	1.2	1.1	123.0	28.6	2.5	17.70	627
MeTic-4	< 0.1	<0.2	< 1	3050	374000	7590	142	48	0.6	2.1	< 0.02	0.1	35.1	55.8	19.1	1.23	376
MeTic-5	< 0.1	<0.2	< 1	3140	355000	12300	190	30	0.4	2.5	< 0.02	0.2	104.0	82.2	17.5	1.01	81
LA6-1	6.9	n.c.	1	4	361	102	63400	42	10.1	2.1	17.1	67.3	17.4	16.9	7.0	15.70	90
Cuc Duong-1	0.1	1.3	143	470	53000	8660	608	1440	7.1	24.6	< 0.02	0.7	63.2	104.0	2.6	8.94	47000
Cuc Duong-3	0.3	1.5	497	1180	132000	1070	781	152	3.1	5.1	< 0.02	1.5	21.6	40.8	6.8	10.00	87100
Cuc Duong-6	0.1	0.8	427	749	83900	173	532	152	2.3	4.2	< 0.02	1.2	11.6	23.7	4.7	16.20	82700
Cuc Duong-8	< 0.1	n.c.	16	17	2330	19	8	18	1.2	2.9	< 0.02	1.4	0.5	2.2	0.5	17.90	97700
Cuc Duong-9	0.3	1.0	839	1780	196000	928	1310	42	4.4	2.8	0.0	1.2	33.1	42.7	10.6	10.40	63300
Cuc Duong3-2	0.2	4.6	27	244	29000	5810	57	51	4.8	5.0	0.1	1.1	32.9	261.0	2.2	7.86	33700
CL-1	1.2	62.4	441	280	12900	22500	451	13300	3.3	5.2	< 0.02	0.5	132.0	120.0	4.6	14.30	3780

n.c., not calculated (Zn contents less than 5,000 ppm)

Appendix 2 Analytical result of Li-Mg to Nb-W of the Pb-Zn ores from northern Vietnam.

Appendix-2

Analyte Symbol	Mg (%)	Li	V	Cr	Al (%)	Ca (%)	Na (%)	K (%)	Rb	Cs	Sr	Ba	Ga	Ge	Tl	Zr	Hf	Be	Nb	W	
Detection Limit	0.01	0.5	1	0.5	0.01	0.01	0.001	0.01	0.2	0.05	0.2	1	0.1	0.1	0.05	1	0.1	0.1	0.1	0.1	
<b>Ha Giang Province</b>																					
Na Son-14	4.53	4.3	39	44	4.29	12.70	0.096	2.03	110	1.4	34	80	18.4	0.1	0.4	34	1.1	4.5	4.1	3.0	
Na Son-35	2.16	8.5	69	49	7.19	2.95	0.171	3.66	224	3.4	16	123	31.9	0.3	0.8	52	1.6	7.9	9.0	31.8	
Na Son-36	1.03	6.2	2	28	4.76	3.19	0.056	4.43	236	1.3	17	70	37.2	0.6	0.7	488	13.5	6.6	88.0	1.3	
Na Son-37	0.80	2.5	23	69	1.87	1.38	0.069	0.59	34	0.5	5	6	36.8	8.9	0.3	67	1.6	1.9	6.0	3.6	
Na Son-38	0.38	4.9	2	23	2.94	0.48	0.030	2.16	126	1.3	1	<1	48.1	0.3	0.6	259	6.6	5.6	9.9	<0.1	
<b>Bac Kan Province</b>																					
Sy Binh-1a	0.09	0.7	<1	2	0.07	0.21	<0.001	0.02	2	0.2	2	2	5.70	0.1	<0.05	1.0	<0.1	<0.1	<0.1	4.3	
Sy Binh-1d	0.32	1.7	3	6	0.34	0.70	<0.001	0.18	22	1.1	7	11	4.90	0.1	0.1	6.0	0.2	0.2	0.9	8.8	
Ba Bo, Cho Don	1.10	7.8	32	27	3.03	4.02	0.093	1.05	129	4.8	62	<1	22.2	0.1	0.9	24	0.6	0.8	1.5	0.8	
Na Tum, Cho Don	0.24	1.5	6	32	0.17	0.10	0.001	0.01	1	0.1	1	<1	27.2	0.3	0.1	82	0.1	0.3	0.3	<0.1	
Na Bop-3, ditto	1.67	3.0	4	12	0.44	20.20	0.003	0.11	18	0.8	152	<1	3.2	0.1	1.1	3	<0.1	0.5	<0.1	<0.1	
Na Bop-4, ditto	0.15	1.5	3	34	0.38	0.32	0.008	0.08	8	0.5	4	<1	3.2	0.1	1.4	9	0.2	0.4	<0.1	<0.1	
Na Bop-24, ditto	2.04	47.7	86	63	7.76	20.60	0.205	3.71	312	51.5	750	467	18.4	0.1	2.3	9	0.2	4.5	9.8	16.8	
Na Bop1610, Cho Don	0.81	8.2	31	22	2.27	1.16	0.031	0.90	192	19.7	22	6	42.6	0.2	1.4	10	0.3	1.5	2.8	32.1	
Na Bop1611, ditto	0.17	3.8	5	5	0.34	0.07	0.004	0.04	3	0.3	1	1	2.7	0.4	0.1	12	<0.1	0.1	0.7	41.9	
Na Bop1612, ditto	0.18	3.6	2	3	0.22	0.33	0.003	0.08	14	1.6	5	1	5.8	0.2	2.2	2	<0.1	0.2	0.2	0.2	
Na Bop1613, ditto	0.12	3.0	5	8	0.29	0.04	0.002	0.03	3	0.2	1	<1	9.3	0.1	0.3	54	0.1	0.2	0.8	5.5	
Na Bop1614, ditto	0.89	2.8	3	6	0.28	3.79	0.007	0.07	6	0.3	30	5	1.6	<0.1	0.1	88	<0.1	0.1	0.3	0.3	
Na Bop1615, ditto	0.31	1.4	7	7	0.69	1.07	0.003	0.05	4	0.4	4	136	2.8	0.2	<0.05	4	<0.1	0.1	0.6	4.6	
Na Bop1616, ditto	1.82	51.2	112	18	1.47	0.24	0.014	0.89	401	60.0	7	13	13.8	0.2	0.3	122	0.4	0.5	2.1	60.7	
Cho Dien 1601	0.80	2.5	7	8	0.66	4.03	0.006	0.25	23	1.3	17	20	1.8	<0.1	0.4	7	0.1	0.1	0.5	2.1	
Cho Dien 1602A	0.74	2.5	7	11	0.60	3.72	0.007	0.23	22	1.0	15	6	1.6	0.1	0.3	7	0.1	0.1	0.7	2.2	
Cho Dien 1602B	0.34	13.4	10	6	0.79	2.09	0.008	0.10	7	0.8	18	6	3.9	0.1	0.2	7	0.1	0.1	1.3	24.4	
Cho Dien 1603	0.14	1.6	4	2	0.18	1.83	0.002	0.06	4	0.4	11	2	1.8	0.2	0.1	9	0.2	<0.1	0.5	36.9	
Cho Dien 1604	0.41	<0.5	6	1	0.04	2.54	<0.001	0.04	3	0.2	17	<1	2.9	<0.1	<0.05	3	<0.1	<0.1	1.0	9.7	
Cho Dien 1605	0.03	0.9	2	<0.5	0.31	0.03	0.006	0.05	8	0.6	2	5	4.9	<0.1	<0.05	<1	<0.1	<0.1	<0.1	4.3	
Cho Dien 1607	0.78	15.0	45	47	3.50	4.23	0.032	2.17	152	7.1	104	136	18.8	0.3	0.6	124	3.1	1.6	4.5	36.0	
Cho Dien 1608	0.68	2.0	6	5	0.32	2.79	0.005	0.13	12	0.8	25	13	5.5	0.1	0.4	7	0.1	0.2	0.7	2.8	
Cho Dien-5	0.26	1.1	10	40	0.24	0.69	0.003	0.04	3	0.5	3	2	2.6	0.1	0.1	5	0.1	0.2	0.2	1.1	
Cho Dien-6	1.12	5.5	6	60	0.53	4.97	0.003	0.04	3	0.2	19	6	2.2	0.1	0.1	206	0.1	0.6	0.5	1.5	
Cho Dien-7	4.43	2.8	20	64	1.61	30.30	0.005	0.62	56	3.6	64	42	4.5	<0.1	0.5	21	0.5	0.8	2.8	3.3	
Cho Dien-8	0.97	0.8	3	11	0.06	12.40	0.001	0.01	1	0.2	109	2	0.2	0.1	0.1	50	0.2	0.4	0.1	1.1	
Cho Dien-26	0.12	2.7	14	29	0.35	0.51	0.015	0.09	7	1.2	11	8	5.1	0.1	0.1	6	0.2	0.5	1.4	11.8	
Cho Dien-27	1.06	4.7	7	50	0.56	7.76	0.007	0.08	7	0.4	33	15	2.7	0.1	0.1	97	0.1	0.5	0.5	2.4	
<b>Thai Nguyen Province</b>																					
Phudo1617	0.06	0.5	11	12	0.85	1.94	0.005	0.48	37	2.0	11	16	26.8	4.7	0.9	72	1.9	0.2	5.6	4.2	
Phudo1618	0.01	<0.5	4	3	0.17	0.87	0.002	0.10	6	0.5	4	20	12.2	2.4	0.3	9	0.3	<0.1	0.6	2.2	
Phudo 1619	0.23	<0.5	1	4	0.11	9.87	0.003	0.05	4	0.4	554	54	2.1	<0.1	0.1	2	<0.1	<0.1	<0.1	<0.1	
Lang Hich-9	0.86	<0.5	3	28	0.07	2.02	0.007	<0.01	0	0.2	2	<1	1.0	6.9	0.4	4	0.1	0.3	0.1	0.4	
Lang Hich-10	0.40	<0.5	5	26	0.27	1.58	0.002	0.05	4	0.5	3	<1	1.5	2.6	1.0	3	0.1	0.3	<0.1	0.2	
Lang Hich-11	0.59	<0.5	1	83	0.08	2.22	0.002	0.01	1	0.4	6	<1	1.6	7.1	3.0	8	0.3	0.4	0.1	0.1	
Lang Hich-12	2.42	1.2	13	52	1.04	4.07	0.008	0.38	29	1.7	43	16	5.6	1.0	0.3	6	0.2	0.6	1.1	0.8	
Lang Hich-13	1.38	1.8	27	23	2.76	4.90	0.022	1.06	78	4.3	12	<1	7.7	3.4	0.9	18	0.5	0.7	2.3	0.8	
Lang Hich-30	0.15	<0.5	1	5	0.01	0.38	0.005	<0.01	0	0.1	1	<1	0.9	13.2	0.3	3	0.1	0.4	0.3	3.3	
Lang Hich-31	0.16	<0.5	2	7	0.19	0.46	0.003	0.04	3	0.3	1	<1	1.1	0.4	0.7	3	0.1	0.3	0.2	1.4	
Lang Hich-33	1.89	1.4	15	29	1.17	5.57	0.008	0.50	37	2.1	34	4	5.9	3.5	0.4	10	0.3	0.6	1.7	2.0	
Lang Hich-34	1.13	0.8	17	22	1.65	4.84	0.014	0.62	48	2.7	5	<1	4.9	2.3	0.6	13	0.4	0.5	1.7	1.0	
Lang Hich-51	5.57	2.0	15	16	1.10	29.30	0.012	0.44	30	1.9	266	46	3.1	0.3	1.5	6	0.2	0.9	0.1	<0.1	
Lang Hich-52	3.85	4.2	47	63	3.36	21.80	0.020	1.18	82	8.5	150	51	8.5	0.4	3.8	34	0.9	1.2	1.0	<0.1	
MeTic-1	2.07	<0.5	6	9	0.06	6.12	<0.001	0.03	1	0.1	44	2	0.50	<0.1	0.2	3.0	<0.1	0.1	<0.1	0.2	
MeTic-2	0.17	<0.5	3	3	0.02	0.38	<0.001	0.01	1	0.1	1	<1	1.70	1.7	0.4	1.0	<0.1	<0.1	<0.1	0.6	
MeTic-3	1.52	<0.5	3	3	0.05	3.82	<0.001	0.02	1	0.1	5	<1	0.80	0.2	0.1	8.0	<0.1	<0.1	0.2	4.6	
MeTic-4	0.08	<0.5	1	2	0.01	3.80	<0.001	0.01	2	0.1	14	1	2.80	8.8	0.3	1.0	<0.1	<0.1	<0.1	1.5	
MeTic-5	0.08	<0.5	<1	4	0.01	1.76	<0.001	0.01	1	0.1	2	<1	2.70	10.8	0.4	1.0	<0.1	<0.1	<0.1	0.6	
LA6-1	0.02	2.6	2	3	0.24	0.03	<0.001	0.11	6	0.3	2	5	1.40	0.2	0.3	4.0	0.1	0.1	0.2	30.5	
Cuc Duong-1	0.39	7.0	21	16	1.12	0.65	<0.001	0.52	51	3.5	8	40	4.30	0.2	0.4	26.0	0.5	0.5	2.0	12.9	
Cuc Duong-3	0.89	4.4	3	5	0.22	0.69	<0.001	0.11	9	0.7	4	8	2.70	0.2	0.1	4.0	0.1	0.1	0.2	5.2	
Cuc Duong-6	1.54	1.7	6	6	0.25	3.10	<0.001	0.12	12	0.7	11	9	3.00	0.3	0.1	8.0	0.2	0.2	0.6	3.6	
Cuc Duong-8	1.55	4.9	3	3	0.21	0.97	<0.001	0.11	9	0.5	2	7	1.40	0.3	0.1	3.0	0.1	0.1	0.2	4.9	
Cuc Duong-9	0.88	1.8	3	3	0.20	1.01	<0.001	0.09	8	0.5	4	6	4.40	0.1	0.1	4.0	0.1	0.1	0.2	4.0	
Cuc Duong3-2	2.30	3.2	12	6	0.41	4.94	<0														



Chemical characteristics of lead-zinc ores (Ishihara et al.)

Appendix 3 Analytical result of Th-U and REE of the Pb-Zn ores from northern Vietnam.

Appendix-3

Analyte Symbol	Th	U	La	Ce	Pr	Nd	Sm	Eu	LREE	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	HREE	ΣREE	
Detection Limit	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.05		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1			
<b>Ha Giang Province</b>																					
Na Son-14	10.8	2.7	30.6	59.1	7.1	30.7	4.9	1.13	133.53	5.9	0.9	4.3	22.5	0.8	2.1	0.3	1.6	0.2	38.6	172.1	
Na Son-35	17.6	4.3	64.7	120.0	13.8	45.3	8.1	1.68	253.58	8.6	1.3	5.7	32.5	1.1	2.6	0.3	1.5	0.2	53.8	307.4	
Na Son-36	60.2	13.8	245.0	454.0	56.2	186.0	32.3	2.13	975.63	33.8	5.2	25.7	131.0	5.9	16.1	2.1	12.6	1.7	234.1	1209.7	
Na Son-37	10.0	2.2	6.1	12.3	1.5	5.4	1.0	0.21	26.51	1.2	0.2	0.9	5.7	0.2	0.5	0.1	0.3	<0.1	9.1	35.6	
Na Son-38	18.3	5.8	67.0	162.0	20.8	71.4	12.5	2.68	336.38	12.2	1.8	8.9	46.2	2.0	5.5	0.7	4.5	0.6	82.4	418.8	
<b>Bac Kan Province</b>																					
Sy Binh-1a	0.2	0.1	0.1	0.3	0.1	0.2	0.1	<0.05	0.8	<0.1	<0.1	0.1	0.30	<0.1	0.1	<0.1	<0.1	<0.1	0.5	1.3	
Sy Binh-1d	1.3	0.3	0.2	1.3	0.2	0.7	0.2	<0.05	2.6	0.2	<0.1	0.3	2.00	0.1	0.3	<0.1	0.2	<0.1	3.1	7.0	
Ba Bo, Cho Don	5.9	1.2	4.3	11.6	1.6	5.8	1.1	0.56	24.96	1.3	0.2	1.2	6.8	0.3	0.9	0.1	0.9	0.1	11.8	36.8	
Na Tum, Cho Don	1.4	0.7	124.0	178.0	23.5	74.2	8.8	1.24	409.74	6.2	0.5	1.4	4.7	0.2	0.3	<0.1	0.1	<0.1	13.4	423.1	
Na Bop-3, ditto	0.7	0.2	18.9	31.0	3.3	10.0	1.3	0.58	65.08	1.2	0.1	0.5	3.2	0.1	0.3	<0.1	0.2	<0.1	5.6	70.7	
Na Bop-4, ditto	0.9	0.9	<0.1	3.2	0.6	2.4	0.6	0.15	6.95	0.7	0.1	0.5	3.3	0.1	0.3	<0.1	0.2	<0.1	5.2	12.2	
Na Bop-24, ditto	12.5	3.7	29.1	55.9	6.7	22.6	3.6	0.74	118.64	3.5	0.5	2.5	16.1	0.6	1.8	0.3	1.5	0.2	27.0	145.6	
Na Bop1610, Cho Don	2.5	1.6	8.6	12.7	1.3	4.2	0.6	0.14	27.54	0.4	<0.1	0.3	1.5	<0.1	0.1	<0.1	0.1	<0.1	2.4	29.9	
Na Bop1611, ditto	0.8	0.3	<0.1	0.3	<0.1	0.1	<0.1	<0.05	0.40	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.5	
Na Bop1612, ditto	0.8	0.2	20.3	25.3	2.6	7.5	0.9	0.15	56.75	0.7	<0.1	0.2	0.6	<0.1	<0.1	<0.1	<0.1	<0.1	1.5	58.3	
Na Bop1613, ditto	0.6	1.4	0.7	0.9	0.1	0.4	0.1	<0.05	2.20	0.1	<0.1	0.1	0.7	<0.1	<0.1	<0.1	<0.1	<0.1	0.9	3.1	
Na Bop1614, ditto	0.6	0.2	6.0	7.0	0.7	1.9	0.3	0.43	16.33	0.3	<0.1	0.4	2.1	<0.1	0.2	<0.1	0.2	<0.1	3.2	19.5	
Na Bop1615, ditto	1.8	0.5	41.6	55.0	5.2	14.0	1.2	0.99	119.99	1.1	<0.1	0.2	1.0	<0.1	<0.1	<0.1	<0.1	<0.1	2.3	122.3	
Na Bop1616, ditto	1.6	1.2	1.3	2.4	0.4	1.6	0.3	<0.05	6.00	0.3	<0.1	0.3	1.6	<0.1	0.2	<0.1	0.1	<0.1	2.5	8.5	
Dien 1601	2.9	0.6	6.2	9.1	1.0	3.3	0.6	0.37	20.57	0.7	0.1	0.6	4.2	0.1	0.3	<0.1	0.3	<0.1	6.3	26.9	
Dien 1602A, ditto	1.8	0.4	4.8	7.2	0.8	2.9	0.5	0.32	16.52	0.6	<0.1	0.6	3.7	0.1	0.3	<0.1	0.3	<0.1	5.6	22.1	
ChoDien 1602B	1.9	0.6	10.8	21.1	2.3	7.8	1.2	0.31	43.51	0.9	0.1	0.5	2.8	0.1	0.2	<0.1	0.2	<0.1	4.8	48.3	
Cho Dien 1603	0.5	0.6	1.9	3.4	0.3	1.0	0.2	0.19	6.99	0.1	<0.1	<0.1	0.5	<0.1	<0.1	<0.1	<0.1	<0.1	0.6	7.6	
Cho Dien 1604	<0.1	1.4	0.6	1.0	0.1	0.4	<0.1	0.19	2.29	<0.1	<0.1	<0.1	0.4	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	2.7	
Cho Dien 1605	0.4	0.2	0.9	2.0	0.2	0.6	<0.1	<0.05	3.70	<0.1	<0.1	<0.1	0.6	<0.1	<0.1	<0.1	<0.1	<0.1	0.6	4.3	
ChoDien 1607	9.0	1.8	25.6	45.5	4.8	16.3	2.7	0.67	95.57	2.2	0.3	1.7	10.7	0.4	1.1	0.2	1.2	0.2	18.0	113.6	
Cho Dien 1608	1.3	0.9	2.3	4.6	0.5	1.7	0.4	0.09	9.59	0.3	<0.1	0.2	1.3	<0.1	0.2	<0.1	0.1	<0.1	2.1	11.7	
Cho Dien-5	0.6	6.0	0.4	0.8	0.1	0.2	<0.1	<0.05	1.50	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	1.7	
Cho Dien-6	0.8	0.3	4.9	8.5	0.9	2.7	0.4	0.45	17.85	0.5	0.1	0.4	2.8	0.1	0.3	0.1	0.4	0.1	4.8	22.7	
Cho Dien-7	4.0	1.7	2.8	5.9	0.7	2.2	0.4	0.17	12.17	0.4	0.1	0.3	1.7	0.1	0.2	<0.1	0.2	<0.1	3.0	15.2	
Cho Dien-8	0.3	0.9	4.4	7.3	0.9	2.8	0.4	0.42	16.22	0.5	0.1	0.3	3.3	0.1	0.2	<0.1	0.2	<0.1	4.7	20.9	
Cho Dien-26	2.5	4.9	22.6	33.5	3.4	8.1	0.6	0.14	68.34	0.4	<0.1	0.1	0.7	<0.1	0.1	<0.1	0.1	<0.1	1.4	69.7	
Cho Dien-27	1.2	0.4	8.1	12.4	1.2	3.8	0.6	0.68	26.78	0.6	0.1	0.5	3.0	0.1	0.3	0.1	0.3	<0.1	5.0	31.8	
<b>Thai Nguyen Province</b>																					
Phudo1617	6.7	2.7	1.9	3.6	0.3	0.9	0.2	<0.05	6.90	0.2	<0.1	0.3	1.9	<0.1	0.3	<0.1	0.4	<0.1	3.1	10.0	
Phudo1618	0.3	0.9	<0.1	0.3	<0.1	0.1	<0.1	<0.05	0.40	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	0.6	
Phudo 1619	0.2	0.4	0.9	1.3	0.2	0.5	<0.1	<0.05	2.90	0.1	<0.1	<0.1	0.6	<0.1	<0.1	<0.1	<0.1	<0.1	0.7	3.6	
Lang Hich-9	0.1	1.3	<0.1	0.1	<0.1	0.1	<0.1	<0.05	0.20	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	
Lang Hich-10	0.3	0.5	<0.1	0.9	0.1	0.4	0.1	<0.05	1.50	0.1	<0.1	0.1	0.4	<0.1	<0.1	<0.1	0.1	<0.1	0.7	2.2	
Lang Hich-11	0.3	0.3	<0.1	0.3	<0.1	0.2	<0.1	<0.05	0.50	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	0.7	
Lang Hich-12	0.7	1.6	0.6	1.3	0.1	0.6	0.1	<0.05	2.70	0.2	<0.1	0.1	0.8	<0.1	0.1	<0.1	0.1	<0.1	1.3	4.0	
Lang Hich-13	3.4	2.5	4.3	9.3	1.1	3.4	0.4	0.10	18.60	0.5	0.1	0.5	3.7	0.2	0.6	0.1	0.7	0.1	6.5	25.1	
Lang Hich-30	0.2	1.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.05	0.20	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	
Lang Hich-31	0.3	0.6	<0.1	0.9	0.1	0.2	<0.1	<0.05	1.20	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	1.2	
Lang Hich-33	1.0	1.5	1.7	3.4	0.4	1.3	0.2	0.05	7.05	0.2	<0.1	0.2	1.4	0.1	0.2	<0.1	0.2	<0.1	2.3	9.4	
Lang Hich-34	2.1	1.3	1.6	4.9	0.6	1.9	0.3	0.08	9.38	0.3	0.1	0.4	2.4	0.1	0.4	0.1	0.5	0.1	4.4	13.8	
Lang Hich-51	1.4	1.6	4.7	10.1	1.4	5.1	1.0	0.24	22.54	1.1	0.2	0.9	5.7	0.2	0.6	0.1	0.5	0.1	9.4	31.9	
Lang Hich-52	5.9	4.9	14.6	26.2	3.1	10.3	1.6	0.37	56.17	1.7	0.3	1.4	9.2	0.4	1.1	0.2	1.1	0.2	15.6	71.8	
MeTic-1	0.7	7.0	0.2	0.5	0.1	0.3	0.1	<0.05	1.2	0.1	<0.1	0.1	0.50	<0.1	<0.1	<0.1	0.1	<0.1	0.8	2.0	
MeTic-2	0.4	1.1	<0.1	0.1	<0.1	0.1	<0.1	<0.05	0.2	<0.1	<0.1	<0.1	0.10	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.3	
MeTic-3	0.5	10.9	0.1	0.3	<0.1	0.2	<0.1	<0.05	0.6	<0.1	<0.1	0.1	0.40	<0.1	<0.1	<0.1	<0.1	<0.1	4.1	4.7	
MeTic-4	0.3	0.7	3.5	6.7	1.1	3.5	0.8	0.2	15.8	0.7	0.1	0.6	3.80	0.1	0.2	<0.1	0.1	<0.1	5.6	21.4	
MeTic-5	0.2	0.7	<0.1	0.2	<0.1	0.1	0.1	<0.05	0.4	<0.1	<0.1	0.1	0.30	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	0.8	
LA6-1	0.3	0.1	0.2	0.4	0.1	0.2	0.1	<0.05	1.0	0.1	<0.1	0.1	0.90	<0.1	0.1	<0.1	0.1	<0.1	1.3	2.3	
Cuc Duong-1	3.0	0.8	12.3	22.9	3.3	10.3	1.9	1.8	52.5	1.8	0.2	1.5	9.60	0.3	0.8	0.1	0.7	0.1	15.1	67.6	
Cuc Duong-3	0.4	0.1	1.0	3.4	0.7	3.3	1.4	1.0	10.8	1.5	0.2	1.2	7.00	0.2	0.5	0.1	0.3	<0.1	11.0	21.8	
Cuc Duong-6																					